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TOXICITY OF THE OFF-GAS PRODUCTS FROM  
DIVER HOSES

Naval Civil Engineering Laboratory  
Port Hueneme, California

October 1970

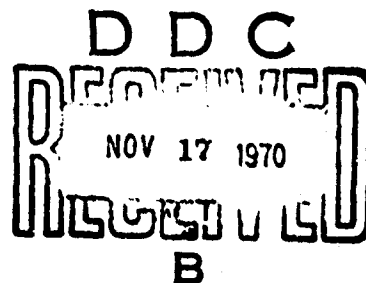
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R 698

Technical Report

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FROM DIVER HOSES

October 1970



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NAVAL CIVIL ENGINEERING LABORATORY

Port Hueneme, California

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# TOXICITY OF THE OFF-GAS PRODUCTS FROM DIVER HOSES

Technical Report R-698

71-007

by

H. P. Vind and C. W. Mathews

## ABSTRACT

The Naval Civil Engineering Laboratory (NCEL) was requested to ascertain the composition and toxicity of compounds off-gassing from diver hoses and to develop new acceptance tests for the military specifications for diver hoses. A literature survey disclosed that the off-gassing would consist primarily of organic solvents and would contain only traces of plasticizers and deterioration products of rubber. Two acceptance tests were developed at NCEL for measuring the quantities of organic solvents emitted by diver hoses. The equipment used can be purchased for between \$2,000 and \$3,000. In both tests, measurements of ionizable carbon are employed as indices of the concentrations of solvent vapors and related organic compounds. In the first test, measurements are made of the carbon content of air confined in the hoses for at least 7 days. Concentrations of up to 50 mg/m<sup>3</sup> are permitted. In the second test, measurements are made of the carbon content of air flushed through the hoses at a rate of 3 ft<sup>3</sup>/min. Concentrations of not more than 0.01 mg/m<sup>3</sup> per foot of hose or a maximum concentration of 4 mg/m<sup>3</sup> regardless of hose length are permitted. The concentration of nearly any compound that might off-gas from diver hoses should be at safe levels in breathing mixtures delivered through hoses that pass the above tests. Exceptions are the solvents carbon disulfide and carbon tetrachloride. Military specifications must forbid their use in the fabrication of diver hoses.

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Total Hydrocarbon Analyzer						
Organic carbon						
Breathing mixtures						
Carbon disulfide						
Carbon tetrachloride						
Carbon tetrachloroethane						
Rubber additives						
Solvents						
Flow rate						
Sulfur compounds						
Recycle test						
Flush test						

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## INTRODUCTION

The Supervisor of Salvage, Naval Ship Systems Command (NAVSHIPS), assigned the Naval Civil Engineering Laboratory (NCEL) the responsibility to ascertain the composition and toxicity of compounds off-gassing from diver hoses and to develop new acceptance tests for the military specifications<sup>1</sup> for diver hoses.

## PREVIOUS STUDIES ON OFF-GASSING OF MATERIALS

### Diver Hoses

No record could be found of fatal poisonings by fumes off-gassing from diver hoses, and no record could be found of investigations on the chronic effects of continued exposure to hose ingredients.<sup>2</sup> However, there are numerous accounts of divers complaining of hoses with obnoxious or nauseating odors.

In 1958 the Experimental Diving Unit (EDU) at the U.S. Naval Gun Factory purchased a number of diver hoses that smelled strongly of rubber cement and were unsatisfactory for use. They flushed one of the hoses with water for 24 hours but it still had an objectionable odor. They sent a 20-foot section of one of the hoses to the Naval Applied Science Laboratory (NASL), for examination.<sup>3,4</sup>

Chemists at NASL flushed the hose with contaminant-free nitrogen for 24 hours, passing the effluent nitrogen through a dry ice trap where the volatile contaminants were condensed and collected. They then examined the condensate by means of infrared spectrophotometry and gas phase chromatography. Their examination disclosed that the principal substances off-gassing from the hoses were toluene, xylene, and tetramethylthiourea disulfide. The first two contaminants are solvents for rubber cements, and the latter is a curing agent for modifying the properties of rubber. It has a very objectionable odor.

The same three contaminants were also evolved from numerous other samples of natural and synthetic rubber hoses and tubing, usually at a lower level than from the objectionable hoses; but they were not evolved from



samples of the rubber stocks from which the hose and tubing were fabricated. The odoriferous contaminants were apparently introduced during the fabrication of the hose or tubing. NASL chemists concluded that objectionable vapors in diver hoses can best be eliminated by judicious selection of hose ingredients and fastidious fabrication procedures. The factory producing the offending hoses followed the recommendation and modified their procedures to minimize residual solvents.

Hoses have also been known to contaminate the breathing mixtures of Navy divers with vapors of fluorinated hydrocarbons. Scientists at the Naval Research Laboratory (NRL)<sup>6</sup> traced the vapor to organic solvents of the Freon type which were used for cleaning hoses according to the Nortronics procedure.<sup>6</sup> The procedure was designed primarily for cleaning metal components of diving equipment, but apparently on a few occasions it was used for cleaning rubber hoses.

The NRL scientists found that hoses which were washed with Freon-113 (1,1,2 trichloro-1,2,2 trifluoroethane) deteriorated rapidly and contaminated the divers' breathing mixtures with solvent vapors. Air held in the hoses for 24 hours acquired a Freon concentration of 4,300 ppm. Furthermore, the Freon removed nonvolatile plasticizers from the hoses, thereby altering their physical properties. The NRL scientists recommended that diver hoses be cleaned with aqueous TSP (trisodium phosphate) solution rather than with organic solvents.

### **Space Cabin Materials**

Several studies have been made on the off-gassing of materials employed in the construction of space cabins. Postinger<sup>7</sup> and Back<sup>8</sup> reported briefly on the off-gassing from 55 candidate space cabin materials. The major off-gas products from polymeric materials were organic solvents. Smaller quantities of plasticizers and monomers and traces of degradation products also appeared in the off-gassing from polymers.

Off-gassing of materials was also studied in the special test chamber of the Integrated Life Support System at Langley Research Center.<sup>9</sup> Ten materials were selected for the study. They consisted of various types of plastic tubing, insulation materials, and metal foil adhesive tapes. Except for trace constituents, the off-gassing at 200°F consisted of organic solvents. The trace constituents were probably plasticizers and thermal breakdown products. The solvents included carbon tetrachloride and other poisonous halogenated organic solvents.

## Trace Contaminants In Submarines

Since the advent of nuclear submarines, scientists have thoroughly investigated the composition of the interior atmospheres of submarines.<sup>10-16</sup> They have presented a great deal of information on trace contaminants in submarines, but aside from showing that vapors from paints and paint thinners are sometimes the principal contaminants in submarine atmospheres, very little information has been published on the off-gassing of specific materials.

In the early history of the analysis of nuclear-submarine atmospheres, it became apparent that the atmospheres were contaminated by a very complex mixture of organic compounds. Freons, methane, carbon monoxide, hydrocarbon vapors, and numerous low molecular weight alcohols, ketones, ethers, and chlorinated hydrocarbons accounted for nearly all of the contaminants. The Freons were identified as refrigerants, and the organic vapors as fuels, lubricants, and commercial solvents. Methane and carbon monoxide were probably primarily of metabolic origin.

The hydrocarbon fraction was so complex that the early effort to routinely monitor the concentrations of individual hydrocarbons in submarine atmospheres was abandoned. The concentrations of gaseous Freons, methane, carbon monoxide, carbon dioxide, oxygen, and nitrogen were still monitored individually; but the vapors of hydrocarbon solvents and miscellaneous alcohols, ketones, and other low molecular weight compounds to which the flame ionization detector is sensitive were monitored collectively as a fraction. The fraction was called "total hydrocarbons" even though it contained compounds which are not strictly hydrocarbons and it did not include methane.

At one time the concentration of the total hydrocarbons in submarine atmospheres frequently rose to  $100 \text{ mg/m}^3$  and occasionally even higher. Strict control of painting, smoking, and other activities that might contaminate the interior atmospheres of the submarines has significantly lowered the level of total hydrocarbons in submarines. According to some of the latest figures<sup>16</sup> released for public information,  $16 \text{ mg/m}^3$  is now more typical. (If we assume that the contaminants are pentane, the carbon content would be about  $13 \text{ mg/m}^3$ ).

## TOXICOLOGY OF ROSE MATERIALS

### Solvents

In all of the enumerated studies, organic solvents were the principal constituents in the off-gassing from polymeric materials. This could have been anticipated from their low boiling points and high solubility in polymeric materials.<sup>17-18</sup>

Some of the industrial solvents most widely used for rubber are listed in Table 1. For each solvent, Table 1 lists the Threshold Limit Value (TLV),<sup>19</sup> which is defined as that concentration of airborne substance to which workers can be exposed for daily periods of 8 hours, 5 days a week, without adverse effects. The far right-hand column of Table 1 gives the expected analyzer reading in mg/m<sup>3</sup> for the carbon content of gas containing the TLV concentration of the listed contaminant. The expected reading on the instrument is not always the same as the actual value because a flame ionization detector is not 100% efficient for all compounds. The values were calculated from estimated efficiencies (Table 2) of flame ionization detectors for the atoms of different classes of compounds.

The most toxic organic solvents that might be employed in the fabrication of the hoses are carbon disulfide, carbon tetrachloride, and tetrachloroethane. Benzene is also very toxic, and other aromatic hydrocarbons are moderately toxic. On the other hand, aliphatic and alicyclic hydrocarbons are toxic only in relatively high concentrations. The lower the boiling point of a solvent of any class, the more readily it will evaporate and be desorbed from a hose.

### Plasticizers

The vapor pressures of all the commercial plasticizers<sup>20</sup> are so low that they pose but little threat of poisoning by inhalation. The higher the boiling point of the rubber plasticizers, the less likely are they to be found in the off-gassing from the rubber. Some plasticizers can form aerosols,<sup>15-16</sup> but the temperatures required to form them are higher than those existing in diver hoses. Of the plasticizers in common use, tricresyl phosphate is by far the most poisonous.<sup>21</sup> Numerous esters of adipic acid are said to be excellent plasticizers for rubber, and they are far less toxic than the phosphate esters.

### Rubber Additives

Literally hundreds of components are added to rubber products at various steps in their manufacture.<sup>22,23</sup> So many different chemicals are added for the same purpose by different formulators at different stages in the fabrication of a rubber product that it is almost impossible to know precisely what it contains.

Many of the rubber additives are very poisonous. Fortunately, with the exceptions of the solvents and plasticizers, most of them are of such limited volatility or they are used in such limited quantities that they off-gas insignificantly. Though many of them frequently cause allergic reactions when they contact the skin, only a few of the rubber additives pose a serious threat of poisoning by inhalation.

Table 1. Threshold Limit Values<sup>a</sup> (TLV) of Industrial Rubber Solvents

Solvents	Boiling Point (°C)	Threshold Limit Values		
		ppm	Actual Carbon Content (mg/m <sup>3</sup> )	Analyzer Carbon Content <sup>b</sup> (mg/m <sup>3</sup> )
Halides				
Carbon tetrachloride	77	10	5	2
Chloroform	61	50	24	15
o-Dichlorobenzene	182	50	147	145
Ethylene dichloride	84	50	40	43
Methylchloroform	74	350	342	280
Tetrachloroethane	147	5	5	4
Trichloroethylene	87	100	98	86
Trichlorotrifluoroethane	46	1,000	974	487
Hydrocarbons (alicyclic)				
Cyclohexane	81	300	892	600
Decahydronaphthalene	190	c	c	c
Methylcyclohexane	101	500	1,714	1,714
Tetrahydronaphthalene	207	c	c	c
Turpentine (oil)	154-170	100	494	494
Hydrocarbons (aliphatic)				
n-Heptane	98	500	1,680	1,680
n-Hexane	69	500	1,505	1,505
Naphtha (petroleum)	30-130	500	1,624	1,624
Gasoline	125	500	1,977	1,977
n-Pentane	36	1,000	2,455	2,455
Hydrocarbons (aromatic)				
Benzene	80	25	74	74
Naphtha	10-100	100	345	345
Toluene	111	300	844	844
Xylene	140	100	304	304
Sulfides				
Carbon disulfide	47	30	9	9
Butylthiocapton	98	15	19	19

<sup>a</sup> Threshold Limit Values of airborne contaminants, adopted by the American Conference of Governmental Industrial Hygienists, 1968.

<sup>b</sup> Estimated from theoretical efficiency of the hydrogen flame ionization detector.

<sup>c</sup> TLV value not yet established but solvent is known to be toxic only in relatively high concentrations.

Table 2. Response of Flame Ionization Detector to Various Atoms in Organic Compounds

Atom	Occurrence	Response <sup>a</sup>
Carbon	in saturated compound	+1.0
Carbon	in aromatic compounds	+1.0
Carbon	adjacent olefinic bond	+0.9
Carbon	adjacent acetylenic bond	+1.3
Chlorine	on aliphatic carbon atom	-0.1
Hydrogen	in all compounds	0.0
Nitrogen	in primary amine	-0.6
Nitrogen	in secondary amine	-0.7
Nitrogen	in tertiary amine	-0.3
Nitrogen	in nitrile	-0.7
Oxygen	in carbonyl radical	-1.0
Oxygen	in carboxyl radical	-0.5
Oxygen	in primary alcohol	-0.6
Oxygen	in secondary alcohol	-0.7
Oxygen	in tertiary alcohol	-0.3
Oxygen	in ether	-1.0
Sulfur	in sulfides	-0.5

<sup>a</sup> Approximate response (for example, effective carbon number) of various atoms relative to a methane molecule as 1.0. The response for a molecule of another organic compound is obtained by adding the estimated responses for its constituent atoms.

There are a few exceptions. Aniline, a frequently used vulcanizing agent is very toxic either when it is breathed or when it is absorbed through the skin. Benzidine and beta-naphthylamine, which are sometimes employed in rubber as "stiffening agents" and antioxidants, are very dangerous carcinogens and in some states are forbidden in any industrial process. Asphalt, creosote, coal tar, and pine tar are frequently used in the reclamation of rubber from used tires. They, too, are carcinogenic.

The number of vulcanization accelerators is large and for the most part they are very toxic organic compounds.<sup>21</sup> The ones used most frequently are mercaptobenzothiazole, tetramethylthiouram disulfide, and tetraethylthiouram disulfide. All three are sensitizers and all have extremely repulsive odors. They evoke allergies on contact with the skin of sensitized individuals; but apparently, in the quantities employed in rubber, they are not dangerous from the standpoint of airborne toxicity. Another accelerator, sulfur monochloride, can

cause *eczematized parakeratoses*, and eczemas are frequently caused by contact with rubber products. Unfortunately, it appears that it is necessary to use at least one of the accelerators in compounding rubber for hoses.

## Rubber

Generally, high polymers such as rubbers are substances of great chemical inertness devoid of physiological and toxicological effects. Some of the monomers of which rubbers are made, however, are very dangerous poisons. In addition to other information, Table 3 gives the TLV values for the principal monomers from which commercial elastomers or rubbers are made.

Pustinger<sup>7</sup> and Back<sup>8</sup> in their investigations of space cabin materials found that the off-gassing from polymeric materials contains traces of unreacted monomers. Lefaux<sup>21</sup> also mentioned that polymers sometimes contain unreacted monomers, but he was discussing thermoplastic polymers rather than elastomers. Apparently polymerization of elastomers is complete and essentially irreversible. Flushing of any of the common types of rubber with water would remove the last traces of unreacted monomer. Pyrolysis and degradation of elastomers generally yield products other than unreacted monomers.

Natural rubber is composed of isoprene units. Neither the polymer nor monomer is toxic. For decades the British Navy has fabricated diver hoses from natural rubber and apparently they have had no problem with off-gassing.

Styrene-butadiene rubber (SBR), also called Government Rubber-Styrene (GR-S), is also synthesized from relatively nontoxic monomers. For several decades most of the diver hoses used by the U.S. Navy have been fabricated of SBR. There have been no incidents of acute poisoning by fumes off-gassing from the Navy hoses. There have only been occasional complaints of obnoxious odors and these have been traced primarily to residual solvents and not to the rubber stocks.

Some of the diver hoses used by the Navy have been fabricated of polychloroprene rubber, for example, Neoprene. Chloroprene is a little more toxic than are the monomers of which natural rubber and SBR are compounded, but unreacted chloroprene has not been reported as an off-gas product of rubber. When polychloroprene rubbers are pyrolyzed or degraded, they liberate the chlorine as hydrochloric acid rather than as monomeric chloroprene.<sup>21</sup> Airborne hydrochloric acid is extremely toxic, but it is readily detected, even in trace concentrations, as a choking and irritating gas. Divers have not complained of a choking and irritating sensation when using hoses fabricated of polychloroprene rubber.

Table 3. Threshold Limit Value (TLV)<sup>a</sup> of Some Well-Known Ingredients and Breakdown Products of Rubber

Compound	Threshold Limit Values			
	ppm	mg/m <sup>3</sup>	Actual Carbon Content (mg/m <sup>3</sup> )	Analyzer Carbon Content <sup>b</sup> (mg/m <sup>3</sup> )
Acrylonitrile	40	70	48	36
Aniline	5	19	15	14
Benzidine	0	0	0	0
Beta-Naphthylamine	0	0	0	0
Butadiene	1,000	2,200	1,954	1,856
Carbon dioxide	5,000	9,000	2,454	0
Carbon monoxide	50	55	24	0
Chloroprene	25	90	49	46
Coal tar pitch volatiles	—	0.2	0.2	0.2
Cresols	5	22	17	16
Ditertiarybutylhydroxytoluene (BHT)	c	c	c	c
Hydrogen cyanide	10	11	5	3
Hydrogen sulfide	10	15	0	0
Isoprene	c	c	c	c
Methylmercaptan	10	20	5	2
Phenyl-Beta-Naphthylamine	0	0	0	0
Styrene	100	420	387	368
Sulfur dioxide	5	13	0	0
Sulfur monochloride	1	6	0	0
Thiram	—	5	1	1
Toluene diisocyanate	0.02	0.14	0.09	0.07

<sup>a</sup> Threshold Limit Values of airborne contaminants, adopted by the American Conference of Governmental Industrial Hygienists, 1968.

<sup>b</sup> Estimated from theoretical efficiencies of the hydrogen flame ionization detector.

<sup>c</sup> TLV has not been established, but compound is known to be relatively harmless. Its use is approved by the FDA for food-handling equipment.

Many of the newer hoses employed by commercial divers are fabricated of polyacrylonitrile rubbers. They have been used for several years, apparently without serious complaints of off-gassing. Monomeric acrylonitrile is a dangerous poison, but it has not been reported as an off-gas product from the rubber. Pyrolysis of polyacrylonitrile rubber yields up to 2% of the even more dangerous hydrogen cyanide. Even at room temperatures hydrogen cyanide can be detected in the off-gassing of polyacrylonitrile rubbers, but the concentrations are so minute that their presence is primarily of academic interest.

Polyurethane rubber is made from toluene diisocyanate (TDI), an extremely toxic substance, but not even traces of TDI can be detected in the off-gassing from polyurethane rubber. The safety of polyurethane rubber is attested to by its popularity for the fabrication of surgical items.

Thus, from the standpoint of objectionable off-gassing, there is no great advantage of one type of rubber over another. The only differences would arise as a consequence of possible differences in the kinds and quantities of solvents, plasticizers, and additives needed for the various rubbers. Other differences in toxicological hazards for the different rubbers might occur if the hoses are overheated or ignited.

## METHODS FOR MEASURING OFF-GASSING

When this investigation began, there was no means other than divers' response for distinguishing noncontaminating diver hoses from those that grossly contaminated divers' breathing mixtures. Military specifications<sup>1</sup> stated, "A sample of hose at least 40 feet but not over 50 feet long shall be used. Any toxic or nauseous effects noted by any four subjects while breathing air passed through the hose for one hour shall be cause for failure of this test."

The test might be satisfactory as a preproduction test, but it is too costly to function as a routine acceptance test. Commercial laboratories charge nearly a thousand dollars to perform the test on a single hose. Another fault is that the compounds most likely to off-gas in quantities harmful to the divers' health are cumulative poisons which have a delayed effect. Even though a subject suffers no discomfort breathing through the hose for an hour, he may accumulate dangerous solvents that will harm his health in later years.

Harris<sup>24</sup> described the test employed in the selection of nonmetallic materials for the Apollo Command Module space cabin. A sample of the candidate material is held at a temperature of 200°F for 48 hours in a test chamber filled with oxygen at 5 psi. At the end of the heating period, a gas sample is drawn off and passed through a gas chromatograph equipped with a flame ionization detector. The total concentration of organic compounds in the sample is expressed as pentane equivalents. Condensable materials are determined by evacuating the test chamber into a cold trap and returning the noncondensables to the test chamber. The test chamber is brought to atmospheric pressure with oxygen and tested for odor by a panel of four trained inspectors. For a material to be acceptable, it must meet the following criteria:

1. The total weight loss, exclusive of water, must be less than 1%.
2. The total organic off-gassing should not exceed 100 ppm by weight when expressed as pentane equivalents (equivalent to a carbon content of 246 mg/m<sup>3</sup>).



3. The material after heating must not have a mean odor exceeding 1.5 on the basis of an olfactometric test in which four panel members rate the odor as:

Not detectable	0
Detectable	1
Objectionable	2
Irritating	3

4. No observable room temperature condensate other than water is obtained.

Again, such a test might be satisfactory as a preproduction test for hoses, but it would be too expensive to serve as a routine acceptance test. It requires several days to perform, and it requires that a short length of the hose be cut off. This would destroy the end-seal on the hoses and permit water to get into the braid.

As already described, NASL tested a hose by trapping the evolved gases in a dry ice trap and then examining the condensate by gas chromatography and infrared spectrophotometry. Various other cryogenic trapping techniques and numerous adsorption techniques have been employed for concentrating contaminants in gas samples prior to their identification. Trace contaminants in submarine<sup>10-16</sup> and SEALAB<sup>25</sup> atmospheres were formerly trapped on carbon black. The contaminants were subsequently desorbed with heat under reduced pressure. Studies at NRL<sup>10-16</sup> show that such trapping methods are inefficient and capture only half of the contaminants. The trapping techniques are also time consuming and are not applicable to on-the-spot analysis. The advent of flame ionization detectors has made possible the direct analysis of trace contaminants in gas streams, and trapping techniques are no longer necessary.

In all of the preceding studies on off-gassing, the off-gas constituents have always been separated or fractionated by gas chromatography. Identity of the chromatographic fractions has been aided by the use of selective sensors,<sup>26</sup> by infrared spectrophotometry,<sup>7</sup> and by mass spectrometry.<sup>7</sup> Only well-equipped research centers are sufficiently specialized to employ such techniques to identify the individual gases and vapors that might be given off by hoses. Furthermore, information is unavailable on the permissible concentrations of many organic compounds likely to be found in the off-gassing from hoses. Hence, for routine testing of diver hoses, it is impractical to identify and measure the concentration of the individual off-gas products.

At NRL considerable effort was devoted to the development of a simple-to-use analyzer for measuring the total concentration of organic contaminants in submarine atmospheres.<sup>10-16</sup> The instrument that was

developed is called the NRL Total Hydrocarbon Analyzer. It is a gas chromatograph with a hydrogen flame ionization detector. This detector is highly sensitive to hydrocarbons and, to a lesser degree, is also sensitive to most other organic compounds (Table 2).

Operation of the NRL Total Hydrocarbon Analyzer involves the use of a technique called "back flushing." A sample of the gas to be analyzed is introduced into the analyzer in the usual fashion and carrier gas is flushed through in the normal direction. After methane and gaseous Freons are eluted, the direction of the carrier gas flow is reversed, and the remaining components are regrouped and eluted as a single "lumped" peak. The area of the peak constitutes the measure of the "Total Hydrocarbon" (minus methane) concentration.

All of the foregoing procedures for detecting off-gas products or other contaminants in gas samples were batch tests. Even the NRL Total Hydrocarbon Analyzer was an instrument for analyzing small gas samples, one at a time. To examine the off-gassing from a hose by such a procedure, a 1-ml sample of gas might be drawn with a gas syringe from near one end of a hose. The sample would then be injected into an analyzer. The contaminants off-gassing from the hose would be ascertained from the composition of the 1-ml sample.

There are serious faults with batch-wise analytical techniques for measuring off-gassing rates. First of all, the concentration of gaseous contaminants in a hose varies considerably from the ends to the center of the hose. Second, the concentration of trace contaminants falls off rapidly as air is flushed through a hose. Finally, even if the sample were representative, nearly all of its trace contaminants would probably be deposited on the sides of the syringe or other sampling device and would not even enter the analyzer. Measuring off-gassing rates from a hose requires an instrument that will handle a continuous sample stream and respond with a continuous reading.

In recent years numerous continuous reading process instruments have been introduced for analyzing streams of gases. They are used in refineries, natural gas lines, and other industrial process plants where it is necessary to continuously monitor the composition of a gas stream. At the present time, instrument makers are engaged in a race to develop process instruments for monitoring air pollution, and new instruments are introduced at frequent intervals.

One of the most successful of the new breed of instruments is a process analyzer for total hydrocarbons. The process analyzers employ a hydrogen flame ionization detector similar to that employed on the NRL Total Hydrocarbon Analyzer. However, the process instrument accommodates a sample stream, whereas the NRL instrument analyzes a single small sample of gas at a time.

Several instrument manufacturers market process analyzers for total hydrocarbons.<sup>27-29</sup> All of their analyzers appear to be ideally suited for monitoring the gross contamination of air by off-gas products from hoses. The analyzers are reliable, extremely sensitive, easy to operate, and respond to most organic compounds. They are moderately priced at approximately \$2,000.

In essence, the Total Hydrocarbon Analyzer counts the number of carbon atoms in the off-gas products from the hoses. It is a little more efficient in counting the carbon atoms in hydrocarbon vapors than in the vapors of other organic compounds, but it responds to nearly all carbon compounds with the exceptions of carbon dioxide, carbon monoxide, and carbon disulfide. The Total Hydrocarbon Analyzer also fails to distinguish between aromatic and aliphatic hydrocarbons.

Infrared<sup>30,31</sup> and ultraviolet<sup>32</sup> process analyzers can also be used to monitor the concentrations of many organic compounds. They are especially well suited for measuring the concentration of carbon dioxide and carbon monoxide, and they can be adjusted for distinguishing aromatic from aliphatic hydrocarbons. Hence, they complement the capabilities of the Total Hydrocarbon Analyzers.

Each infrared or ultraviolet analyzer is sensitive to only one compound or one narrow class of compounds. This is determined by the composition of the gas in the reference cell of the instrument which is filled at the factory. Resistances and other components of the analyzers must be adjusted at the factory to match the reference cell. Such a high degree of specificity reduces the value of the analyzers for measuring the off-gassing from diver hoses. Furthermore, optical instruments like the ultraviolet and infrared analyzers are less sensitive than the Total Hydrocarbon Analyzers. To be useful for detecting trace contaminants in gases, they would need dry ice traps or carbon canisters for concentrating the trace contaminants.<sup>33</sup> Though the optical instruments are essential for monitoring the concentration of carbon monoxide and carbon dioxide in divers' breathing mixtures, they would not be very useful for measuring off-gassing from diver hoses which evolve insignificant quantities of carbon monoxide and carbon dioxide.

Inability of the Total Hydrocarbon Analyzer to detect carbon disulfide is a more serious shortcoming. Carbon disulfide is an excellent solvent for rubber, and its vapors are extremely poisonous.

There are numerous types of analyzers on the market that might be employed for measuring the off-gassing of sulfur-containing compounds from diver hoses. In general there are several makes of each type. Most of the instruments are excellent for their specified purposes, but some appear to be better suited than others for measuring the rate of off-gassing of sulfur compounds from diver hoses.

One popular type of analyzer reduces all sulfur compounds catalytically with hydrogen.<sup>34</sup> The resulting hydrogen sulfide reacts with a moving lead acetate impregnated tape. Discoloration of the tape by lead sulfide is measured continuously with a photocell. Instruments of this type are very specific for sulfur. They have been used very successfully in refineries and natural gas lines. However, they cannot be used for analyzing air or other gas mixtures containing oxygen. If they were used for measuring off-gassing from diver hoses, they would require hydrogen as the carrier gas. The hydrogen required to flush a hose at a rate comparable to the flushing it would receive in use would constitute an explosion hazard of considerable magnitude. Another disadvantage of instruments of this type is that their response is slow, requiring several minutes for equilibrium to be established, and their readout time is even slower because of the time lag for developing the color on the sensitive tape.

A popular type of analyzer<sup>35-37</sup> for measuring the concentrations of sulfur compounds in air employs a liquid electrochemical detector. The air is bubbled through an iodine-iodide or a bromine-bromide solution confined in the electrochemical cell. Sulfur compounds in the air reduce the halogen solutions which are continuously reoxidized electrolytically back to their original oxidative state. Continuous measurements are made of the current required. Various instrument makers employ electrochemical cells of slightly different design.

Instruments of this type are not specific for sulfur compounds but will respond to any agents which are easily oxidized or reduced. Of the agents which are most likely to be off-gassed from rubber hoses, only sulfur compounds are usually detected. The response time is slow and approximately 4 minutes is required for equilibrium to be established each time there is a change in the concentration of sulfur compounds. In comparison to the hydrocarbon analyzer, the range of the electrochemical instrument is rather limited. A hose grossly contaminated with carbon disulfide would cause the instrument to go off scale. Several hours of flushing with contaminant-free air might be required to decontaminate the cell. Finally, fairly large samples are required, and recycling procedures which will be described later in this report cannot be used for evaluating hoses with an electrochemical sulfur analyzer.

Flame photometry appears to be a practical procedure for measuring the concentration of sulfur compounds in air passed through diver hoses. Formerly, flame photometers suitable for continuous analysis of gas mixtures were primarily research instruments, too sophisticated and expensive for routine procedures. However, there has recently become available a simplified analyzer with a flame photometer for continuously monitoring the total concentration of sulfur compounds in gas streams.<sup>38</sup> The instrument is specific for sulfur compounds and detects all of them.

Some chlorinated solvents, especially carbon tetrachloride and tetrachloroethane, are very poisonous, and they have frequently been employed in rubber cements used to fabricate hoses. The hydrocarbon analyzer will detect these agents but at an approximately 50% efficiency as compared to the detection of unsubstituted hydrocarbons. Apparently, no process analyzer is now available for detecting halogen compounds selectively and continuously, but a halogen leak detector might be adaptable for that purpose.<sup>39</sup>

## APPROACH

Toxicologists have not yet agreed upon a permissible value for the total concentration of organic impurities in divers' breathing mixtures. Even if the permissible concentration had been established, it would be next to impossible to state a permissible limit for the rates of off-gassing from diver hoses. Each situation would require a different value because the length of the hose, temperature of the water, length of stay underwater, and numerous other factors would certainly all influence the final value.

Nevertheless, some sort of limit should be set for the rate of off-gassing of organic constituents from diver hoses. Failure to do so is tantamount to stating that anything is acceptable whereas, in fact, even the best is not as good as desired. Stating that no off-gassing is permitted is unrealistic, because all hoses, especially new ones, do off-gas to some extent.

One approach for overcoming the dilemma might be to measure the off-gassing rates of the best available diver hoses and employ those rates as the maximum permissible until better hoses are available and until more is known about the toxicological effects of the off-gas products of hoses. Another approach might be to ascertain the most likely composition of the off-gassing from diver hoses and set limits which would keep the concentrations of the predicted compounds at safe levels.

Both approaches were employed at NCEL. Measurements were made of the off-gassing rates of numerous commercially available hoses. Some idea was thereby obtained of the magnitude of off-gassing limits which industry could practically meet. Then a survey was made of hose technology to ascertain the most likely composition of off-gas products. It was established that the off-gassing from hoses is most likely to consist primarily of hydrocarbon solvents, both aromatic and aliphatic. Permissible limits were established on the assumption that the off-gassing is composed entirely of benzene. The limits were within a range which industry should be able to meet.

## EXPERIMENTAL METHODS AND RESULTS

### Materials and Equipment

All of the hoses, with the exception of one used Navy diver hose, were purchased or supplied new specifically for this investigation. They are briefly described in Table 4. Though they had not been used, many of them had obviously been stored for a long time after they were fabricated. Some of the hoses (Table 4) were supplied with the specific understanding that they were of recent manufacture and had been stored only briefly. Though most of the hoses tested were manufactured for other purposes, they all were types frequently used by divers.

A Beckman Total Hydrocarbon Analyzer, Model 109A, and a Beckman Sulfur Dioxide Analyzer, Model 906, were employed for the tests described in this report. Their use is not to be construed as a recommendation for the use of Beckman instruments over those of other manufacturers.

The Beckman Model 906 Sulfur Dioxide Analyzer comes equipped with a selective filter for removing all of the readily oxidized and reduced contaminants in air with the exception of sulfur dioxide. When the filter is removed, the instrument becomes in essence a total sulfur analyzer.

### Off-Gassing of Organic Carbon Compounds

A great number of measurements were made of the concentrations of organic compounds in streams of helium flowing through hoses at various flow rates. The measurements were made with a Total Hydrocarbon Analyzer. Flow rates as low as 0.1 cfm were employed. The slower the flow rates, the higher were the concentrations of organic contaminants, but a very long time was required to establish steady-state conditions at low flow rates.

Measurements were also made to ascertain the effect of pressure on the off-gassing of hydrocarbons. It was observed that the lower the pressure of air flowing through the hoses at a given flow rate, the greater was the concentration of off-gassing hydrocarbons. However, flow rates were measured in terms of air at standard temperature and pressure. Though the meter indicated that the flow rates were equal at high and low pressure, the volumes of air passing through the hose per unit time were not equal.

It was recognized that contamination would be at a maximum rate when the flushing rate was zero and that a zero flushing rate could be achieved by recycling the same air through the hose in the manner shown in Figure 1. A steady reading was then established in a relatively short time and the results were reproducible on different days or even on different weeks.

Table 4. Some Measurements of the Off-Gassing of Hoses Frequently Used by Divers

No.	Brand	Description of Hose	Composition of Tube <sup>a</sup>	Inside Dimension of Hose (in.)	Length of Hose (ft)	Carbon Content (mg/m <sup>3</sup> )	
						Recycle Test	Flush Test
1	A	British Navy Diver	NR	3/8	60	17	—
2	B	U.S. Navy Diver 1959	SBR	1/2	50	10	1/2
3	B	U.S. Navy Diver 1967	CR	1/2	50	33	2
4	B	U.S. Navy Diver (used) 1961	SBR	1/2	50	6	0
5	B	High pressure diving <sup>b</sup>	NBR	1/2	275	418	32
6	B	General purpose	SBR	1/2	30	21	1
7	C	High pressure diving	NBR	1/2	200	70	3
8	C	High pressure diving <sup>b</sup>	NBR	1/2	200	59	5
9	C	Divers' floating	NBR	1/2	80	14	1
10	C	General purpose	CR	1/2	60	10	2
11	C	General purpose	NBR	1/2	100	8	1/2
12	D	Orchard spray	SBR	3/8	150	130	2
13	E	Hydraulic	Nylon	1/2	50	8	1/2
14	E	Hydraulic	Nylon	3/8	50	10	1/2
15	F	Hose made to Navy Spec	CR	1/2	50	45	1
16	G	Agricultural	SBR	1/2	70	10	1/2
17	G	Agricultural	SBR	3/8	200	16	1
18	H	Agricultural	SBR	1/2	30	10	1
19	H	Agricultural	SBR	3/8	95	5	1/2
20	H	Agricultural <sup>b</sup>	SBR	1/2	100	215	7
21	H	Agricultural <sup>b</sup>	SBR	1/2	100	385	10
22	H	Agricultural <sup>b</sup>	SBR	1/2	100	275	—
23	H	Agricultural <sup>b</sup>	SBR	1/2	100	280	—
24	H	Agricultural <sup>b</sup>	SBR	1/2	100	293	—
25	H	Agricultural	SBR	3/8	100	100	—
26	H	Agricultural	SBR	3/8	100	99	—
27	H	Agricultural	SBR	3/8	100	84	—
28	H	Agricultural	SBR	3/8	100	43	3
29	H	Agricultural	SBR	3/8	100	150	4
30	I	Undersea umbilical <sup>b</sup>	Polyurethane	3/8	200	50	4

<sup>a</sup> NR = Natural rubber

SBR = Styrene Butadiene rubber

NBR = Acrylonitrile Butadiene rubber

CR = Chloroprene rubber

<sup>b</sup> Fabricated recently.

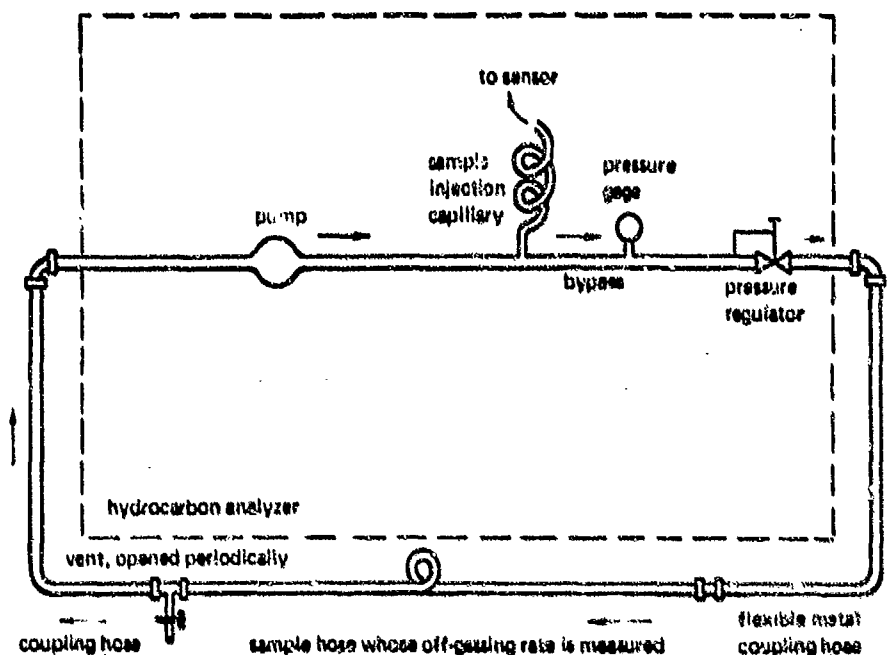


Figure 1. Flow diagram of apparatus for measuring the concentration of hydrocarbons that accumulate in the air confined within a hose.

It was also recognized that the concentrations of off-gassing hydrocarbons would approach a steady state in a relatively brief time if the flushing rate were very rapid. Therefore, the flow rate for the flush tests was increased to 2 cfm. Rather than purified helium, filtered air was employed.

The Total Hydrocarbon Analyzer accommodates a maximum flow rate of about 2 cfm. Therefore, it was necessary to devise a means for sampling only a portion of the air flushed through the hose. The arrangement devised is shown in Figure 2.

Typical results obtained by the recycling and flush tests are given in Table 4. Some of the hoses had perhaps never before been flushed with air or water and some may have been thoroughly flushed or washed. Some may have stood for years before they were flushed. Thus, it would be unfair to compare brands on the basis of the results of Table 4 so brand names are not given.



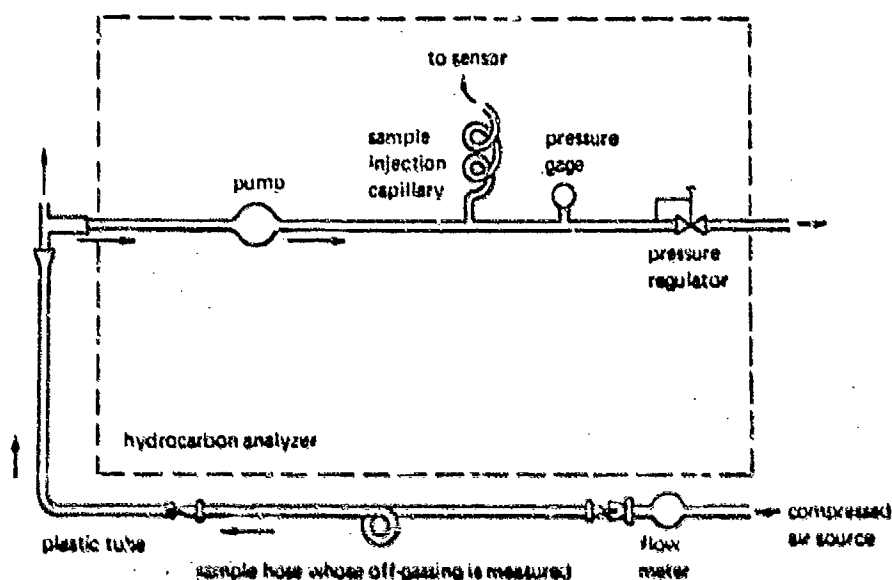


Figure 2. Flow diagram of apparatus for measuring the concentration of hydrocarbons in a stream of air or other gas after it has passed through a test hose.

The data of Table 4 does illustrate that off-gassing varies considerably from hose to hose. Even the results on the two sets of five agricultural hoses, which were supplied at the same time by the same manufacturer and fabricated by the same procedure from the same materials, varied considerably in magnitude.

Hoses no. 5, 8, 20 through 24, and 30 are presumed to have stood the shortest period of time since fabrication. Off-gassing from these hoses is strikingly higher than for those which had been fabricated several years previously. Residual solvents gradually disappear and off-gassing from old hoses is negligible.

Numerous attempts were made to degas hoses that off-gas at high rates. For example, the nitrile rubber high pressure diving hose (no. 5, Table 4) was flushed for 72 hours with 22°C air at 1 cfm. Several recycling tests for hydrocarbons were made at various time intervals thereafter (Table 5). The off-gassing rate of the hose was considerably reduced immediately after flushing, but in time partially regained its initial high level. A 25-foot section of the hose was degassed further while it was submerged in a hot water bath maintained at 57°C. The reduction in off-gassing rate was even greater than had occurred after the 72-hour room temperature flush; but again, the off-gassing rate partially recovered on standing (Table 6).

Table 5. Recycle Test Results for Off-Gassing Rates of Nitrile Rubber Hose

(Flushed with room temperature air at 3 cfm for 72 hours)

Time	Carbon Content (mg/m <sup>3</sup> )
Before flushing	418
Immediately after flushing	10
1 hour after flushing	52
2 hours after flushing	77
24 hours after flushing	193

Table 6. Recycle Test Results for Off-Gassing Rates of a 25-Foot Section of Nitrile Rubber Hose

(Flushed with air at 3 cfm while submerged in water at 57°C)

Time	Carbon Content (mg/m <sup>3</sup> )
Before heating	177
Heated to 57°C	508
Immediately after flushing	2
1 hour after flushing	30
3 days after flushing	52
6 days after flushing	69
8 days after flushing	75
13 days after flushing	80

Other attempts were made to degas nitrile rubber hoses and the results were similar. Flushing the polyurethane hose (no. 30, Table 4) for 7 hours with room temperature air at 3 cfm temporarily reduced the off-gassing rates, but a week later it had returned to its initial level. It seemed a little easier to degas styrene butadiene rubber hoses, and their off-gassing rates gradually fell even if they were not flushed. Drawing conclusions on the relative ease of degassing various rubbers, however, is premature because the experimental

data is too limited, and it was not obtained in directly comparable experiments. Of greater importance than composition of the rubber polymers is no doubt the composition of the solvents. Hoses fabricated with low boiling solvents should be easier to degas.

Because divers use hoses of various lengths, it is important to know whether length of hose influences the test results. One bit of information was obtained from the nitrile rubber hose of the previous discussion. The hose was originally approximately 275 feet long. A 25-foot section was cut from it. A comparison of the results obtained on the two segments of the hose in the standard recycling and flush tests were as follows:

Hose Segment (ft)	Recycle Test for Carbon Content (mg/m <sup>3</sup> )	Flush Test for Carbon Content (mg/m <sup>3</sup> )
250	171	8
25	177	2

Additional information on the influence of length of hose on the results obtained in the standard recycling and flush tests were obtained from measurements made on the two sets of five 100-foot lengths of agricultural hose (no. 20 to 29, Table 4). Measurements were made of the maximum off-gassing rate of each of the hoses by the standard recycling procedure. Flush tests were then made on each of two hoses of each diameter. The three remaining hoses of each diameter were then fastened together to form 300-foot hoses. Measurements of the maximum off-gassing rates of the two 300-foot hoses were made by the standard recycling test. Immediately afterwards they were tested by the standard flush test. The results are summarized in Table 7.

Table 7 shows that results of the recycle test are unaffected by the length of the hose, but that the results of the flush test are proportional to some function of the length. By itself, Table 7 would also indicate that the off-gassing rates of both tests are influenced by the diameters of the hoses. Such an interpretation does not take into account the fact that the hoses of the two diameters were obviously fabricated in different runs, possibly at considerably different times. One would expect the results of the flush test to be affected by hose diameter because it is necessary to move air with a greater velocity through a hose with a small diameter than through a hose with a large diameter. However, there is no reason to expect that hose diameter influences the results in the recycling tests, because in the latter tests a diffusion equilibrium is measured rather than a steady-state function of the flow rate, as is the case with the flush tests.

Table 7. Effect of Hose Length on the Results of the Standard Recycle and Flush Tests

Hose <sup>a</sup> (no.)	Length (ft)	Inside Dimensions (in.)	Carbon Content (mg/m <sup>3</sup> )	
			Recycle Test	Flush Test
20	100	1/2	213	7
21	100	1/2	333	10
22	100	1/2	277	—
23	100	1/2	266	—
24	100	1/2	233	—
20, 21, and 22	300	1/2	290	16
25	100	3/8	106	—
26	100	3/8	99	—
27	100	3/8	84	—
28	100	3/8	43	3
29	100	3/8	150	4
27, 28, and 29	300	3/8	99	6

<sup>a</sup> See Table 4.

### Off-Gassing of Sulfur Compounds

Investigations of the off-gassing of sulfur compounds from hoses was cut short by reductions in funding. A relatively small number of measurements were made, all with the selective filter of the analyzer still in place. Thus, measurements were made of the concentrations of sulfur dioxide rather than of total sulfur. The measurements were performed primarily as a means of becoming better acquainted with the instrument and were to be followed by measurements with the filter removed. The latter measurements were never made.

The sulfur dioxide analyzer required too great a sample flow to permit a recycling test for sulfur. (See recycling test for hydrocarbons under Proposed Acceptance Tests.) The nearest approach was to attach one end of the hose directly to the inlet port of the analyzer and leave the other end of the hose open. The instrument pump drew air through the hose at a rate of 150 ml/min.

In all cases the maximum readings occurred in less than 30 minutes and fell to nearly zero in another 30 minutes or so. The exact time at which the main surge passed through the analyzer varied a great deal and was

influenced by the hose length. If the hoses were permitted to stand a day or two after they had been flushed down to low readings, they regained their capacity to evolve sulfur dioxide. Recovery of off-gassing rates of sulfur dioxide was more rapid than the recovery of the off-gassing rates of hydrocarbons had been.

The foregoing results imply that sulfur dioxide was flushed from the interior rubber surfaces of the hoses and not from deeper layers of rubber. The magnitude of the surge of sulfur dioxide and the time required for recovery of the off-gassing rate were perhaps measures of how rapidly sulfur compounds in the rubber are oxidized.

No measurements were made of the carbon disulfide evolved from the hoses. However, some of the measurements of sulfur dioxide (Table 8) were made with a scrubber filled with a chromic acid solution inserted at the inlet of the analyzer. The scrubber removed an impurity from the hose that was contaminating the electrochemical cell of the analyzer. The scrubber should have converted at least some of any carbon disulfide that might have emanated from the hoses into sulfur dioxide which would have been detected by the analyzer. Apparently none of the hoses tested when the chromic acid scrubber was in position gave off significant quantities of carbon disulfide.

### Off-Gassing of Hydrogen Cyanide

Hydrogen cyanide off-gassed from a hose was trapped in a sodium hydroxide solution and converted to the sodium salt. To ensure that no hydrogen cyanide was allowed into the hose with the air, a trap was also placed at its inlet.

Air was passed through the hose and bubblers at the rate of 1 cfh for 24 hours. Both solutions were then checked for the presence of sodium cyanide.<sup>40</sup> The test method is quite specific and very sensitive.

No cyanide was detected in any inlet trap, but all outlet traps attached to hoses fabricated from acrylonitrile rubber contained sodium cyanide. Hoses made of natural rubber, chloroprene rubber, or styrene butadiene rubber did not off-gas hydrogen cyanide (Table 9). Hose no. 5, which off-gassed the smallest quantity of hydrogen cyanide, was flushed with hot water several months previously for the experiment described in Table 6.

It should be noted that the TLV of hydrogen cyanide (Table 3) is nearly 1,000 times greater than its concentration in air passed slowly through the nitrile rubber hoses.

Table 8. Maximum Concentrations of Sulfur Dioxide in Air Surging Through Diver Hoses

Date	Hose <sup>a</sup> (no.)	Sulfur Dioxide Reading <sup>b</sup> (%)	Dichromate Scrubber
27 Sept	7	42	no
23 Oct	7	40	no
27 Oct	7	37	no
28 Oct	7	20	no
31 Oct	7	39	yes
27 Sept	8	26	no
23 Oct	8	10	no
31 Oct	8	11	no
27 Sept	10	5	no
23 Oct	10	7	no
27 Sept	11	3	no
29 Oct	11	3	no
4 Nov	15	29	yes
4 Nov	21	5	yes
4 Nov	combined 20 to 24	15	yes
17 Nov	30	<1	yes

<sup>a</sup> From Table 4.

<sup>b</sup> 100% = 0.5 ppm sulfur dioxide.

### Off-Gassing of Toluene Diisocyanate

A colorimetric test was devised for detecting toluene diisocyanate in air passed through diver hoses. The test was a simplified version of the test described by Zapp<sup>41</sup> for monitoring air in work areas where polyurethane foam plastics are produced. Filtered air was passed through a bubbler containing a 50-ml aliquot of a reagent solution consisting of 200 ml of 1% aqueous sodium nitrate and 300 ml of ethylene glycol monoethyl ether (Cellasolve). The air was then passed through a hose and finally through a second bubbler

filled with the sodium nitrate-glycol ether solution. The air flow was maintained at a rate of 1 cfh for 24 hours. Off-gassing of toluene diisocyanate by the hose would be indicated by a yellow-orange color in the second bubbler cylinder.

Table 9. Detection of Minute Traces of Hydrogen Cyanide in Air Flushed Through Diver Hoses

Hose <sup>a</sup> (no.)	Composition <sup>a</sup>	Hydrogen Cyanide Content ( $\mu\text{gm}/\text{m}^3$ )
1	NR	0
2	SBR	0
5	NBR	<9
7	NBR	14-1/2
8	NBR	18
8 (repeat)	NBR	27
10	CR	0
11	SBR	0
18	SBR	0

<sup>a</sup> See Table 4.

Although the test for toluene diisocyanate is not as specific as is the test for hydrogen cyanide, it is a very sensitive test. Not even a minute trace of toluene diisocyanate could be detected off-gassing from the polyurethane hose (no. 30, Table 4) and none of the others were tested.

## RECOMMENDATIONS

It is recommended that the military specifications for diver hoses be revised to include the following statements.

### Organic Solvents

The organic solvents used at any stage in the fabrication of a diver hose, including the solvents used for the rubber cements for fastening couplings to the hose, for sealing or capping the ends of the hose, for

bonding the layers and plies of the hose together, or for any other application which might contribute to the contamination of an air stream passing through the hose, shall conform to the following specifications.

The solvents shall be composed of one or more saturated aliphatic or alicyclic hydrocarbons. They shall contain less than 0.1% by weight of aromatic hydrocarbons (suggested method: ASTM-D1017) and less than 0.001% by weight of sulfur (suggested method: ASTM-1266). The solvents shall contain no carbon tetrachloride, tetrachloroethane, or carbon disulfide. Restrictions on use of the aromatic solvents, benzene, toluene, and xylene, shall be waived if the total off-gassing is sufficiently low (see Eecycle Test under Proposed Acceptance Test), but the restrictions on carbon tetrachloride, tetrachloroethane, and carbon disulfide remain in effect.

### **Rubber Additives**

So that the hose may be as free from odor as possible, it shall be fabricated of rubber containing the minimum quantities necessary of the purest commercial grades of accelerators, both in the cover and tube. The rubber shall contain neither phosphate plasticizers nor aniline. No processing aide, extender, or plasticizer having an aromatic hydrocarbon content of greater than 100 ppm (ASTM-D107) or known to have a TLV<sup>19</sup> of less than 25 ppm may be added. Neither benzidine, sometimes employed as a stiffening agent for rubber, nor beta-naphthylamine, sometimes employed as an antioxidant for rubber, shall be used at any stage in the manufacture of diver hoses. Derivatives of beta-naphthylamine (for example, phenyl-beta-naphthylamine) shall also not be employed. It is recommended that antioxidants of the phenolic type, such as ditertiarybutylhydroxytoluene (BHT), be used rather than aromatic amines.

### **Lubricants and Gasket Dressing**

Coupling lubricants and gasket dressings shall be employed only in very limited quantities. Only highly purified silicone oil or U.S.P. petrolatum may be used.

### **Proposed Acceptance Tests**

It is proposed that air hoses for military divers be tested by means of a Beckman Model 100A, a Foxboro, or an M-S-A Total Hydrocarbon Analyzer or any equivalent process analyzer employing a flame ionization detector and having a capacity to detect contaminating carbon at levels



ranging from 0 to 200 mg/m<sup>3</sup>. The preceding term designates the mg/m<sup>3</sup> of carbon contained in that concentration of methane which will cause the instrument to give the same reading (Tables 1 and 3). The flame ionization detector of the Total Hydrocarbon Analyzer is sensitive not only to hydrocarbons but to related organic compounds (for example, see Table 2).

The measurements shall be made only on hoses which have never been flushed with air, gas, or water, or which have been stored at a temperature not lower than 22°C for a period of at least 7 days since they were flushed. During the 7-day storage period the ends of the hoses shall either be sealed shut or fastened together so that the confined gas may not escape. Both the analyzer and the hoses shall be maintained at a temperature not lower than 22°C throughout the testing period.

The procedures for measuring off-gassing rates from hoses are described below as the recycle test and the flush test. The recycle test shall be performed first. Both procedures can be used for measuring the off-gassing rates of hoses of any reasonable length—for example, 25 to 600 feet. Equipment for the tests can be purchased for between \$2,000 and \$3,000.

**Recycle Test.** Air is more highly contaminated when it flows slowly through a hose than when it flushes rapidly. Maximum contamination occurs when the flushing rate is zero. Simply moving or recycling air through a hose, out one end and right back into the other, does not flush the hose but merely mixes the air. The contaminants all remain in the hose and are recycled with the air. Therefore, the maximum level to which air is contaminated by a hose (at a given temperature) can be conveniently measured by continuously recycling the air through the hose, the analyzer, and back through the hose. The measurement should be relatively unaffected by the length or diameter of the hose, or by the rate of recycling of the air.

During the recycle test, one end of the hose is connected to the bypass outlet of the analyzer and the other end is connected to the sample inlet (Figure 1). The instrument pump forces the air or gas confined within the hose to recycle through the hose and analyzer. With the Beckman instrument it recycles at a rate of approximately 0.7 to 1.2 l/min (1-1/2 to 2-1/2 cfm), but the actual rate is not critical.

Five to 10 ml of gas per minute escape through the sample capillary to the flame. To prevent loss of pressure, the hose is periodically briefly vented to the atmosphere. Venting once every 15 minutes is sufficiently frequent to prevent pressure drop in hoses 100 to 200 feet long. More frequent venting is necessary for shorter hoses, and no venting is needed during a 30-minute test period for hoses 400 feet or more in length.

Measurements of the carbon content of the air, expressed as  $\text{mg}/\text{m}^3$ , are recorded every few minutes (or continuously with a recorder) for a period of 30 minutes. Readings for the first 10 minutes may vary considerably. A reading which falls steadily even after the first 10 minutes usually indicates that there is a major leak at a coupling or elsewhere in the line. A reading which steadily rises usually indicates that equilibrium conditions have not yet been attained since the previous flushing of the hose. In a normal test the readings either become steady after the first 10 minutes or they fluctuate up and down, within relatively narrow limits, as a pocket of gas periodically passes through the analyzer. The hoses are rated by the average reading over the last 20 minutes according to the following scale:

<u>Rating</u>	<u>Carbon Content (<math>\text{mg}/\text{m}^3</math>)</u>
Acceptable	0 to 50
Conditional	50 to 100
Unacceptable	>100

Hoses with a conditional rating are acceptable if neither benzene nor any other solvent having a TLV with a carbon content of less than  $100 \text{ mg}/\text{m}^3$  (Table 1) was used in the fabrication of the hoses. If the rating is acceptable, restrictions on the use of benzene may be waived; but the use of carbon disulfide, carbon tetrachloride, and tetrachloroethane must still be forbidden.

**Flush Test.** By this procedure, measurements are made of the increase in the carbon content of a stream of air flushed through the hose at a velocity of  $85 \text{ l}/\text{min}$  ( $3 \text{ ft}^3/\text{min}$ ). The temperatures of the hose, air supply, and analyzer shall not be less than  $22^\circ\text{C}$ . A diagram of the flow arrangement is given in Figure 2.

Before it passes through the hose, the air should be clean and should have a carbon content of not more than  $1 \text{ mg}/\text{m}^3$ . The analyzer is zeroed with air passing at the stipulated velocity through the connector tubes only. The hose is then inserted in the line and the air stream flushed through it. For the ensuing 15 minutes, readings of the hydrocarbon concentration are recorded every few minutes (or continuously with a recorder). The hoses are rated on the reading at the end of the 15-minute test period. Hoses which cause a greater increase in the carbon content of the air stream than  $0.01 \text{ mg}/\text{m}^3$  per foot of hose or a maximum of  $4 \text{ mg}/\text{m}^3$  regardless of length are unacceptable.

## CONCLUSIONS

The proposed acceptance tests do not guarantee that the concentrations of carbon tetrachloride, tetrachloroethane, and carbon disulfide are at safe limits in the off-gassing from diver hoses. Fortunately, price essentially eliminates the likelihood that tetrachloroethane will be used in the fabrication of hoses. Price also certainly curtails the use of carbon tetrachloride and carbon disulfide because they are a little more expensive than hydrocarbon solvents. Another factor is that safety personnel have been striving for decades to eliminate the use of these two solvents. Both are very toxic and carbon disulfide is so inflammable that it ignites spontaneously at 125 to 135°C. Even contact with a warm steam pipe or electric light may cause it to ignite. Thus, the likelihood that carbon tetrachloride, tetrachloroethane, or carbon disulfide will be employed in the fabrication of diver hoses is not very great. The concentrations of any other compounds likely to be off-gassed should be at safe levels in breathing mixtures flowing through hoses that pass the proposed acceptance tests.

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